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STUDIES ON THE INFLUENCE OF CHROMIUM COMPOUNDS ON
THE BIOLOGICAL TREATMENT OF EFFLUENT IN
THE PRESENCE OF TANNERY EFFLUENT

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STUDIES ON THE INFLUENCE OF CHROMIUM COMPOUNDS ON THE BIOLOGICAL
TREATMENT OF EFFLUENT IN THE PRESENCE OF TANNERY EFFLUENT
[Untersuchungen über den Einfluss von Chromverbindungen auf die
biologische Abwasserbehandlung in Gegenwart von Gerbereiabwasser]

By

G. Königfeld,
West German Tannery School at Reutlingen, Research and
Development Department

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The objective of the studies was to determine the concentrations at which chromium compounds contained in tannery effluents would have detrimental effects on biological sewage treatment in the activated sludge and anaerobic digestion processes. It was found that in the normal operating range of an activated sludge plant (pH 7.0-8.5), the chromium concentration can be increased to at least 500 mg Cr (III)/l effluent without any detrimental biological effects. In a properly designed anaerobic digester plant, the concentration can be at least 3200 mg Cr (III)/l sludge (in the form of the oxide) without interfering with the biology. This means that the limit of 4 mg dissolved and undissolved Cr per liter of raw effluents established in the "Guidelines for Introducing Effluent from Commercial and Industrial Facilities into a Public Sewage System" is too low, but this should not restrain the leather industry from doing its best to keep the chromium concentration in leftover liquor as low as possible.

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The question of the toxic effects of tannery effluents and their constituents on biological sewage treatment and on the utilization of sludge in agriculture is not just a water problem of general interest, but also a source of very serious financial obligations for the leather industry. In order to classify the currently vital problems of water economy as comprehensively and uniformly as possible, the Husmann committee in West Germany has formulated the "Guidelines for Introducing Effluent from Commercial and Industrial Facilities into a Public Sewage System" [1]. These guidelines are not compulsory regulations, but were just intended to indicate the degree of purity to which the individual branches of industry could and should purify their effluent before emptying it into a public sewage system. Supposedly, the price for this degree of purity would not be exorbitant.

These guidelines provide that the concentration of trivalent chromium compounds, dissolved or undissolved, should not exceed 4 mg Cr/l raw effluent. Previous experience indicates, however, that this limit is so low that it will be very difficult to adhere to. Of course, improved consumption of tanning liquor in chromium tanning has been the subject of many experiments [2] in recent years as part of comprehensive studies on increasing the efficiency of wet work in leather production. Substantial progress has been made by work on short baths and by varying the operating conditions. However, even under these conditions, the concentrations exceed the limit given in the "Guidelines" by a wide margin. The only way to meet this limit would be to subject the chromic-ion-containing leftover tanning liquor to a completely separate internal cleaning process before it was mixed with tanning effluents from other stages of production. However, intensive studies in recent years have shown that eliminating the chromium salts originating in the leather factories

would be highly uneconomical from the viewpoint of recovering and regenerating them as chromium tanning salts [3], even though it sometimes is or has to be done, usually on the orders of the sewage authorities. Furthermore, there is still a great deal of controversy on whether such a large-scale removal of chromium compounds from the leftover liquors of the leather industry as that given in the "Guidelines" is always, or even ever, necessary. Therefore, before the leather factories are obliged to set up a very costly special cleaning process for the chromium tanning liquors, it was decided to check whether the concentration limit established by the Husmann committee is really necessary.

The studies were therefore intended to determine the effects of various concentrations of dissolved and undissolved chromium compounds in the effluents of the leather industry, in combination with other sewage, on biological purification, sludge digestion, and utilization of sludge in agriculture. This report presents results only on experiments dealing with the influence of chromium compounds in activated sludge plants and in sludge digestion. A special report will be made on the studies concerning the utilization of chromium-containing sludges in agriculture. Furthermore, it was only the effects of compounds of trivalent chromium which were investigated, since compounds of hexavalent chromium, which are known to be much more toxic, are virtually absent from tanning effluents. As the normal case, it can be assumed that the tanning effluent is treated together with domestic sewage in community or district treatment plants, after it has been previously homogenized in a settling tank at the factory. However, there will also be cases in which e.g. a favorable location with respect to a main sewage ditch will make the construction of an independent treatment plant appear appropriate.

The mixed effluents from leather factories can contain the chromium compounds in the following forms:

1. As soluble chromium compounds. They leave the chromium tanning process in this form, but are largely precipitated in the mixing tank (see next paragraph). Hence, the concentrations of soluble chromium compounds in the mixed effluents are relatively small.
2. Precipitated as chromium hydroxide or highly basic chromium salts, which are also more or less covered with oil and thus are quite resistant to redissolving in a weakly acidic reaction (e.g. in illegal drainage of acidic effluents or acidic inversion during biological treatment). Since the pH of the mixed effluent must be between 6.5 and 9.5 according to the Guidelines of the Husmann committee, and since the optimum point of chromium precipitation is also roughly in this pH range (7.5-9.5), the majority of the chromium compounds can be anticipated to be in insoluble form.
3. Bound to hide substance, e.g. in the form of tanned hide fibers, buffing dust, etc. This chromium can be released from its bonding to the hide substance in the degradation of the organic hide substance during biological treatment. However, under the pH conditions in the sludge, it is immediately converted to chromic hydroxide.

The majority of the chromium compounds present in the effluent from a tannery are therefore insoluble, and thus go automatically into the primary sludge and thus directly into the sludge digestion, but a small fraction can get into the activated sludge plant in dissolved or perhaps undissolved form. We have therefore studied the influence of the chromium compounds in all these three forms and for both stages.

A. Literature Survey

There is extensive literature on the questions posed in this work, but the information they provide is very contradictory. Hence, they contain only limited evidence and do not furnish any clear answers. Frequently, results obtained just in one single case are blithely generalized without allowing for the fact that the other constituents may have favorable or unfavorable effects on the given conditions, so that the results attributed to the presence of chromium compounds could also be brought about by other constituents. The following review includes only publications dealing with the influence of trivalent chromium compounds in tannery effluents on biological treatment, in particular the activated sludge process and sludge digestion.

1. Activated Sludge Process

As mentioned above, the literature figures on the toxicity of chromium compounds for the biology of sewage treatment are very contradictory, even with respect to the activated sludge process. In this case, the figures for detrimental concentrations are sometimes on the order of magnitude of the "Guidelines" of the Husmann Committee, while other references state that trivalent chromium compounds are essentially harmless for the activated sludge process.

For instance, I.F. Laboon [4], in an old article, gives a maximum concentration of 3 mg Cr/l in the effluent if organic material is to be degraded in a biological sewage-treatment plant. At a meeting of the Northampton Group (England) in 1970, dealing with the problems of biological purification of mixed residential and industrial sewage in the city of Northampton and including a discussion of tannery effluents [5], it was stated that activated sludge plants were probably sensitive to chromium contents greater than 5 mg Cr/l,

particularly when there were sudden chromium "surges" of higher concentrations. K.W. Pepper [6] also stated that the activated sludge treatment is sensitive to chromium, although community sewage-treatment plants do not suffer any ill effects when up to 10% of their input is sewage from chromium tanneries for periods of several weeks. D.A. Bailey, J.J. Dorrell, and K.S. Robinson found [7] that adding 15 mg Cr/l to effluent intended for the activated sludge process had no detrimental effects on the biological activity of the plant concerned. The authors particularly pointed out that most of the trivalent chromium in tannery effluent does not reach the biological treatment stage at all, but is removed as primary sludge in the initial sedimentation treatment, while the small amounts being carried over into the activated sludge plant would certainly not cause any difficulties. Furthermore, it was found that these small amounts of chromium are removed as excess sludge, thus substantially enhancing the precipitation properties of the activated sludge. In 1969, the US Department of Health [8] reported that the harmlessness limit when a purification plant was subjected to prolonged or suddenly applied trivalent chromium loads was 50-80 mg Cr/l.

On the basis of their work, a number of authors have arrived at the view that the trivalent chromium from leather factories is practically harmless for community treatment plants. These include Heukelekian [9], Humphreys [10], Moore et al. [11], and R. Köhler [12, 13], the latter stating that there is enhanced absorption of chromium in biological treatment, since the activated sludge can take up as much as 18.4% chromium by dry weight. W. Frendrup and H.G. Scholz [14] also found that the mixed, i.e. homogenized, effluents of a leather factory do not obstruct the biological reaction, since in that case, the chromium compounds occur as hydroxide flakes because of the neutral or

alkaline pH, and thus do not enter the biological reaction, as was already suggested in some of the references cited. Lastly, L. Oger and R. Lasserre [15] expressed similar views.

2. Sludge Digestion

Evidence in the literature on the influence of trivalent chromium compounds on sludge digestion is just as inconclusive and contradictory as in the field of activated sludge treatment. The lowest levels alleged to be harmful were given by C.R. Hoover [16] and by W.S. Wise [17], according to whom even 1 mg Cr/l in raw sewage could impair sludge digestion because chromium compounds gradually concentrate in the effluent sludge; on the other hand, according to A.D. Caster [18] and S.E. Coburn [19], the chromium level must be at least 5 mg Cr/l before sludge digestion is impaired. V.A. Barash [20] gives a limit of 50 mg Cr/l. According to A.E.I. Pettet [21], it takes 200 mg Cr/l to influence the rate of digestion. According to the findings of K.W. Pepper [6], the addition of up to 300 mg Cr/l trivalent chromium in the form of an unmasked chromium tanning agent over a period of 28 days had no influence on sludge digestion or methane output.

Extensive investigations dealing with the influence of trivalent chromium on the biological treatment of residential sewage had already been conducted by the previously mentioned team of English authors [7], who also studied the conditions in sludge digestion in great detail. They made the following interesting findings:

"A concentration of up to 300 mg Cr/l in fresh sludge does not cause any difficulties in digestion tanks with residence times of 21, 28, and 35 days.

"Employing a residence time of 17 days, 50 mg Cr/l cause no difficulties; 100 mg Cr/l in the fresh sludge bring about a reduction by 8%

in gas production, but the operation was satisfactory in other respects. With a residence time of 14 days, the reduction in effectiveness became appreciable, when the concentration of chromium in the sludge was greater than 50 mg Cr/l, but operation with a diminished gas yield was possible all the way up to a maximum concentration of 90 mg Cr/l. If the gas were not going to be used immediately as an energy source, this situation would have to be tolerable."

According to R. Vrijburg [22], 500 mg Cr/l in the sludge reduces by half the gas yield in 10 days of digestion.

The next group of reports give results in percentages. For instance, S. Velten [23] states that the chromium content could be more than 2%, in terms of the dry weight of the sludge, without having a substantial influence on sludge digestion. However, he relies primarily on a work of M. Strell [24] of the Bavarian Biological Laboratory, who came to the conclusion that a chromium content of 2.386% by dry weight before beginning gasification experiments or about 3% by dry weight after terminating these experiments did not hinder gasification, although he did not exclude the possibility that the decomposition (gasification) of the organic parts of the sludge might be limited by gradual concentration of the chromium in the sludge. In her book, Gewerbliche und industrielle Abwässer, Entstehung, Schädlichkeit, Verwertung, Reinigung und Beseitigung [Commercial and Industrial Effluents -- Origin, Harmfulness, Utilization, Purification, and Removal] [25], Miss Sierp discusses the problem of mixing tannery effluent with residential sludge:

"When two parts tannery sludge were mixed with three parts sludge from the Munich urban sewage-treatment plant, he obtained proper digestion with a satisfactory gas yield. He mixed the sludge digested in this fashion with fresh tannery sludge in a 1:1 ratio. A chromium content of 3% by dry weight in the tannery sludge did not interfere in these digestion experiments."

According to R. Köhler [12, 13, 26], studies showed that it takes concentrations of 5% chromium by dry weight to disturb the digestion process. A Polish study on tannery effluents by S. Perkowski [27] also states that the

gas output of the digestion is reduced to some extent by the introduction of leftover chromium liquor from the tannery. Lastly, the Proceedings of the 64th Annual Meeting of the Association of American Tanners [28], in which the complete is made that the sewage authorities "do not distinguish between tri-valent and hexavalent chromium, although the former is harmless."

In all, however, previous studies are not sufficient to provide conclusive answers to these questions, since the conflicting evidence precludes a really reliable judgment. Therefore, further systematic studies with unequivocally analyzable experimental runs were necessary.

1. Activated Sludge Experiments

The activated sludge process currently plays an important role in biological treatment of sewage. Experiments will be undertaken with the objective of determining the amounts of chromium salts which may be added to sewage in dissolved or undissolved form without giving rise to difficulties in the activated sludge method, the course of which is known to depend on the healthy activity of a very diverse group of microorganisms. Furthermore, the activated sludge method is particularly well suited for biological model experiments, primarily because it leads more quickly to conclusive evidence with the simplest experimental accessories. The experiments were carried out in an apparatus developed by the "Industrial Sewage Working Group" (Rüsselsheim am Main). In essence, the setup is derived from the detergent test assembly [29].

Fig. 1 shows the model apparatus employed. The arrangement consists of a storage tank for the effluent (not shown in the drawing) which is pumped in at (1); a twin pump (P, P₁) with motor; two initial aeration tanks (2, 7); two aeration units (8); a biological reactor for the biological degradation (3);

a settling tank (4) with a sludge return pipe (6); and a water outlet (5). The effluent employed was the synthetic effluent prescribed in the Regulation on the Degradability of Detergents [29]. For this effluent,

3750 mg peptone (from casein)

2500 mg meat extract

650 mg urea

150 mg sodium chloride

100 mg calcium chloride 2 H₂O

50 mg magnesium sulfate 7 H₂O

are dissolved in one liter of nutrient solution. This stock solution, prepared fresh daily, was diluted to 24 l as prescribed with Reutlingen water. Activated sludge from the biological treatment system of the Reutlingen urban collection and purification plant was used as the inoculating sludge, which was practical whenever the removed sludge was to be kept no longer than 1 h without aeration. Immediately after it arrived in the laboratory, this activated sludge was aerated. In accordance with the directions for the device, the entire quantity of sludge was thoroughly mixed and one liter was allowed to sit for precisely 30 min. The sediment volume was then to be 400 ml/l. If the sludge volume was greater, as usually occurred, the activated sludge was appropriately diluted with fresh water to the desired sediment volume of 400 ml per liter.

Before setting each series of experiments in motion, the inoculating sludge prepared in this way was modified so that initially the volume of the biological reactor (3) was adjusted by means of a cylindrical insert or by appropriately regulating the height of the overflow siphon following the settling tank (4) to 17 liters. In the large, empty aeration vessel (3) prepared

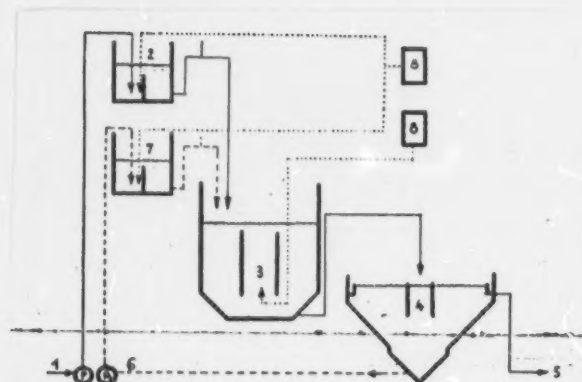


Fig. 1. Model apparatus for activated sludge experiments.

in this fashion, half of the set volume (i.e. 8.5 liters) was filled with diluted activated sludge according to the appropriate directions. The remaining half of the volume was then filled over the course of about 14 hours (overnight) by the pump (P) delivering the synthetic effluent at a suitably slow rate. Both the initial aeration tank (2) and the biological reactor (3) were aerated continuously and vigorously by two separate aerators. By the next morning, the tank (3) was essentially filled to the overflow volume (17 liters) and the liquid was running out of the aeration vessel into the settling tank. The output of the pump P was then set so that about 24 liters passed through the entire apparatus over a period of 24 hours. Shortly before the settling tank (4) had filled, and the purified water could flow off toward (5), the sludge return pump P_1 , which pushed the sludge back through the pre-aeration vessel (7) into the activation tank (3), was switched on and likewise set to a delivery of 1 liter per hour. Each morning, the water flowing out at (5) over the previous 24 hours was mixed well, drawn from the drainage tank, and employed for the desired analytical studies. After the adaptation of the sludge, which normally took place in 2 days, the chromium compounds intended

for the individual experiments were added, in this case directly to the aeration tank (3). Otherwise, nothing in the above operation (pump delivery, aeration intensity, etc.) was changed.

To determine the impairment of the biological purification effect, the potassium permanganate consumption was measured every day in the output water. Moreover, this water was tested for the presence of chromium and for its pH. Furthermore, the temperature in the activation tank was measured every day, although practical experience has shown that temperature fluctuations, as long as they are not extreme, but remain within normal limits as in the experiments conducted here, are relatively unimportant for aerobic fermentation. Naturally, the potassium permanganate consumption of the synthetic effluent was measured before it was added to the biological reactor, the values given in the tables "at the beginning" of the experiment representing in each case the mean values for the synthetic effluent prepared fresh daily.

1. First Series of Experiments with Chromosal B

In this series of experiments as in further studies, Chromosal B was employed as a prototype of a commercial 33% basic chromium sulfate frequently employed in the leather industry. The results in Table 1 cover five separate studies, each experiment using freshly procured purified sludge. The chromium added to the effluent was

in Experiment 1	5 mg,
in Experiment 2	10 mg,
in Experiment 3	25 mg,
in Experiment 4	50 mg,
and in Experiment 5	100 mg Cr/l effluent.

Table 1

Series of experiments with Chromosal B

Messungen a.	b.		c.		d.	
	in synth. Abwasser	in Klarwasser- ablauf	Verbrauch (mg/l) e.	pH-Wert f.	in Reaktions- gefäß	Temp. (°C)
Versuch 11 mit 5 mg Cr/l						
zu Beginn	163.0	-	-	-	-	23.9
nach 1 Tag	-	31.5	7.60	-	-	23.7
nach 2 Tag	-	32.7	7.58	-	-	22.6
Chromzugabe	-	-	-	-	-	-
nach 1 Tag	-	32.9	7.49	-	-	22.8
nach 2 Tag	-	31.8	7.52	-	-	23.1
nach 3 Tag	-	32.6	7.48	-	-	22.9
Versuch 21 mit 10 mg Cr/l						
zu Beginn	168.5	-	-	-	-	23.3
nach 1 Tag	-	34.8	7.68	-	-	23.0
nach 2 Tag	-	33.9	7.59	-	-	23.1
Chromzugabe	-	-	-	-	-	-
nach 1 Tag	-	34.5	7.50	-	-	23.4
nach 2 Tag	-	34.1	7.52	-	-	23.1
nach 3 Tag	-	33.5	7.56	-	-	23.2
Versuch 31 mit 25 mg Cr/l						
zu Beginn	165.6	-	-	-	-	23.4
nach 1 Tag	-	39.7	7.35	-	-	23.5
nach 2 Tag	-	39.0	7.49	-	-	23.4
Chromzugabe	-	-	-	-	-	-
nach 1 Tag	-	40.1	7.38	-	-	22.9
nach 2 Tag	-	39.6	7.40	-	-	23.4
nach 3 Tag	-	39.2	7.37	-	-	23.1
Versuch 41 mit 50 mg Cr/l						
zu Beginn	166.0	-	-	-	-	22.7
nach 1 Tag	-	27.6	7.32	-	-	22.5
nach 2 Tag	-	26.9	7.35	-	-	22.0
Chromzugabe	-	-	-	-	-	-
nach 1 Tag	-	26.1	7.21	-	-	22.4
nach 2 Tag	-	27.3	7.26	-	-	22.9
nach 3 Tag	-	27.1	7.34	-	-	22.1
Versuch 51 mit 100 mg Cr/l						
zu Beginn	170.1	-	-	-	-	22.1
nach 1 Tag	-	39.2	7.26	-	-	21.9
nach 2 Tag	-	38.6	7.29	-	-	22.3
Chromzugabe	-	-	-	-	-	-
nach 1 Tag	-	37.9	7.20	-	-	22.7
nach 2 Tag	-	37.8	7.18	-	-	22.5
nach 3 Tag	-	38.9	7.33	-	-	22.1

g. Chromnachweis in Klarwasserablauf stets negativ.

- Key: a. Measurements
 b. In synthetic effluent
 c. In treated water (output)
 d. In activation vessel
 e. Consumption
 f. pH
 g. Chromium determination in treated water output
 always negative.

Versuch = experiment
 mit = with
 zu Beginn = at the beginning
 nach = after
 Tag = day
 Chromzugabe = introduction of chromium

In all experiments, the system operated the first 2 days without any chromium being added, i.e. just with synthetic effluent and with the appropriate inoculating or activated sludge, following which the diluted Chromosal solution was added to the biological reactor (3) over the course of an hour in the required amount. After 3 more days, the experiments were terminated.

The series of experiments were begun with 5 mg Cr/l, because the "Guidelines" of the Husmann Committee provide for a maximum of 4.0 mg Cr/l effluent. As the results of Experiments 1 through 5 of this first series show, even adding 100 mg Cr/l under the given normal pH conditions between roughly 7.2 and 7.6 did not appear to cause any significant harm to the biological activity of the activated sludge in comparison to the corresponding activation system not yet subjected to the chromium load. The resulting treated water was always chromium-free, an indication that the chromium was always present in insoluble form, and thus an absolutely indifferent form, in the activated sludge.

2. Series of Experiments with Chrome Alum

In the same way, a further series of experiments was conducted, merely substituting chrome alum for Chromosal B as the compound suspected of impairing biological processes. Again, five separate experiments were carried out with new activated sludge in each case and with chromium loads of 5-100 mg Cr/l effluent. In this series as well (Table 2), the potassium permanganate consumption figures did not appear to affect the activation process even when 100 mg Cr/l was employed. As expected, chromium was not detected in any of the treated water in the existing pH range of roughly 7.1-7.5.

3. Series of Experiments with Chromosal B and Increasing Amounts of Chromium

Once these experiments had yielded completely negative findings, the following runs were conducted with even greater amounts of chromium. After

Table 2

Series of experiments with chrome alum

Messungen a.	b.	c.	d.
	im synth. Abwasser Verbrauch (mg/l) e.	im Klarwasser- ablauf pH-Wert f.	im Relebung- gefäß Temp. (°C)
Versuch 1: mit 5 mg Cr/l			
zu Beginn	165.6	-	23.6
nach 1 Tag	-	49.0	23.4
nach 2 Tag.	-	48.6	23.6
Chromzugabe	-	-	-
nach 1 Tag	-	48.2	23.1
nach 2 Tag.	-	49.3	23.6
nach 3 Tag.	-	49.3	23.2
Versuch 2: mit 10 mg Cr/l			
zu Beginn	169.2	-	22.5
nach 1 Tag	-	42.6	22.1
nach 2 Tag.	-	41.5	22.6
Chromzugabe	-	-	-
nach 1 Tag	-	43.0	22.8
nach 2 Tag.	-	42.1	22.5
nach 3 Tag.	-	42.9	23.0
Versuch 3: mit 25 mg Cr/l			
zu Beginn	170.1	-	22.4
nach 1 Tag	-	40.1	22.7
nach 2 Tag.	-	39.3	23.4
Chromzugabe	-	-	-
nach 1 Tag	-	39.8	23.5
nach 2 Tag.	-	38.6	22.9
nach 3 Tag.	-	38.0	23.4
Versuch 4: mit 50 mg Cr/l			
zu Beginn	169.6	-	22.9
nach 1 Tag	-	39.6	23.1
nach 2 Tag.	-	39.0	23.2
Chromzugabe	-	-	-
nach 1 Tag	-	39.7	22.9
nach 2 Tag.	-	39.5	22.8
nach 3 Tag.	-	40.6	23.3
Versuch 5: mit 100 mg Cr/l			
zu Beginn	167.3	-	21.8
nach 1 Tag	-	32.8	21.6
nach 2 Tag.	-	31.9	22.0
Chromzugabe	-	-	-
nach 1 Tag	-	31.5	22.4
nach 2 Tag.	-	32.6	22.1
nach 3 Tag.	-	32.0	22.0

g. Chromnachweis im Klarwasserablauf stets negativ

- Key: a. Measurements
 b. In synthetic effluent
 c. In treated water (output)
 d. In activation vessel
 e. Consumption
 f. pH
 g. Chromium determination in treated water output
 always negative.

Versuch = experiment
 mit = with
 zu Beginn = at the beginning
 nach = after
 Tag = day
 Chromzugabe = introduction of chromium

a 2-day blank run without chromium, 100 mg Cr/l was added first in the form of Chromosal B, followed by another 100 mg Cr/l at 2-day intervals, so that the roughly 24-liter volume of the apparatus finally contained 500 mg Cr/l, present in flocculated form, possibly bound to the flakes of activated sludge, under the normal operating and pH conditions of 7.5-7.6. This sludge gradually took on the characteristic green color of chromium hydroxide, although there was no decrease in the biological activity of the sludge even in this experiment with gradually increasing concentrations of chromium in the activation system. The latter follows from the figures on potassium permanganate consumption in Table 3. Chromium was not detected in any of the treated water in this case either.

4. Series of Experiments with Chromium Hydroxide at pH $\approx$ 7.5

In the previous series of experiments with Chromosal B or chrome alum, the dissolved chromium compounds were converted to insoluble hydroxides under the typical effluent pH conditions, and thus were essentially inactivated. Nevertheless, it seemed useful to carry out experiments with aged chromium hydroxide itself, although, as Bailey et al. [7] had already pointed out in their article, most of the trivalent chromium does not reach the biological treatment stage at all, but is removed in advance as primary sludge. After all, it could happen that a technical malfunction in the settling tank ahead of the activated-sludge unit could release certain amounts of flocculated chromium sludge into the biological section. In order to check the effect of such a chromium sludge, a relatively large amount of chromium-hydroxide sludge was prepared from chrome alum by precipitation with sodium carbonate solution, allowed to age for 3 weeks, and then analyzed for its chromium content. Next, in an experiment run with fresh activated sludge, 250 mg Cr/l were first added

Table 3

Series of experiments with Chromosal B and increasing quantities of chromium

Messungen a.	b.			m. Relebens- ref. d.
	in synth. Abwasser KNO ₃ -Verbrauch (mg/l) e.	in Klarwasser- ablauf pH-Wert f.	c.	temp. (°C)
zu Beginn	185,1	-	-	21,8
nach 1 Tag	-	39,5	7,65	21,6
nach 2 Tag.	-	38,9	7,60	21,4
1. Chromzugabe: 100 mg Cr/l				
nach 1 Tag	-	38,4	7,56	21,2
nach 2 Tag.	-	35,2	7,62	21,4
2. Chromzugabe: 100 mg Cr/l				
nach 1 Tag	-	40,1	7,62	21,0
nach 2 Tag.	-	38,6	7,51	21,6
3. Chromzugabe: 100 mg Cr/l				
nach 1 Tag	-	35,1	7,49	21,4
nach 2 Tag.	-	40,1	7,54	21,2
4. Chromzugabe: 100 mg Cr/l				
nach 1 Tag	-	39,5	7,50	21,0
nach 2 Tag.	-	39,0	7,64	21,4
5. Chromzugabe: 100 mg Cr/l				
nach 1 Tag	-	40,6	7,57	21,2
nach 2 Tag.	-	39,3	7,62	21,7
g. Chromnachweis in Klarwasserablauf stets negativ				

Key: a. Measurements
 b. In synthetic effluent
 c. In treated water (output)
 d. In activation vessel
 e. Consumption
 f. pH
 g. Chromium detection in treated water
 always negative

zu Beginn = at the beginning
 nach = after
 Tag = day
 Chromzugabe = introduction of chromium

in the form of the hydroxide, after 2 days without chromium. Throughout the experiment, the pH was held at about 7.5, employing slight adjustments with NaOH if needed. After 3 days, in which the chromium should have become noticeable, 250 mg Cr/l (again as chromium-hydroxide sludge) were added. The results in Table 4 again show that the already oily chromium hydroxide had

practically no influence on the biological activity of the activated sludge, although in this experiment as well, the activated sludge took on completely the color of the chromium hydroxide. This result is not surprising in view of the outcome of Series 3 with increasing chromium concentrations in dissolved form.

Table 4

Experiments with increasing amounts of chromium hydroxide in the pH range about 7.5

Messungen a.	b. in synth. Abwasser	c. in Klarwasser- ablauf	in Relektungs- gefäß d.	
	Chrom- verbrauch (mg/l) e.	pH-Wert f.	Temp. (°C)	
zu Beginn	179.5	-	-	21.0
nach 1 Tag	-	31.4	7.46	21.4
nach 2 Tag.	-	31.0	7.50	21.6
1. Chromhydroxid-Zugabe: 250 mg Cr/l				
nach 1 Tag	-	32.1	7.52	21.1
nach 2 Tag.	-	31.5	7.56	21.4
nach 3 Tag.	-	31.0	7.49	21.2
2. Chromhydroxid-Zugabe: 250 mg Cr/l				
nach 1 Tag	-	31.6	7.45	21.0
nach 2 Tag.	-	31.0	7.50	21.0
nach 3 Tag.	-	31.7	7.54	21.2
g. Chromnachweis im Klarwasserablauf stets negativ				

- Key: a. Measurements
b. In synthetic effluent
c. In treated water (output)
d. In activation vessel
e. Consumption
f. pH
g. Chromium detection in treated water
always negative.
h. Addition of chromium hydroxide

zu Beginn = at the beginning
nach = after
Tag = day

5. Series of Experiments with Chromium Hydroxide in the pH Range Around 6.0

According to M. Strell [30], Cramer and Wilson investigated the influence of hydrogen ion concentration on the activated sludge method and found that

the effectiveness of the activated sludge was reduced both by raising and lowering the pH by significant amounts. The most favorable hydrogen ion concentration corresponds to a pH between 7.2 and 7.4, so that the activated sludge plants should operate in this optimum pH range if possible, practical experience with the biocenosis indicating that the pH is pushed very close to the physiological optimum just by the metabolites of the organisms. In practice, however, a certain drop in pH must be anticipated due to the influx of acidic effluent. Therefore, experiments were conducted in the pH range around 6.0. Normally, this pH will have no fundamental influence on the biological effectiveness of the activated sludge but some chromium ions going into solution might cause a certain impairment of the biology, since the range in which chromium hydroxide is insoluble begins at about 6.5 and has its optimum between 7.5 and 9.5 [31].

The pH of the effluent was adjusted to 6.0 by adding appropriate amounts of sulfuric acid. Otherwise, the procedure was the same as in Series 4 in the pH range around 7.5, i.e. 250 mg Cr/l was first added to the reaction vessel after 3 days, followed by the same amount of chromium in the form of the hydroxide aged for 3 weeks. Whether the somewhat higher potassium permanganate consumption in the overall course of this experiment (Table 5) was connected with the activated sludge employed or whether it was linked to a certain influence of the lower pH remains to be seen. At any rate, it was found that the acidity of the system did not dissolve significant amounts of the chromium hydroxide, so that even these very high amounts of chromium compound had no detrimental effect on the biological treatment.

Table 5

Experiments with rising amounts of chromium hydroxide at a pH around 6.0

Messungen a.	b.	c.	d.	
	in synth. Abwasser KNO ₃ -verbrauch (mg/l) e.	in Klarwasser- ablauf pH-Wert f.	in Relebens- gefäß Temp. (°C)	
zu Beginn	172.8	-	-	22.4
nach 1 Tag	-	50.1	5.92	22.0
nach 2 Tag	-	50.4	5.95	22.2
h. 1. Chromhydroxid-Zugabe: 250 mg Cr/l				
nach 1 Tag	-	52.5	6.11	21.9
nach 2 Tag	-	51.9	6.14	22.1
nach 3 Tag	-	51.8	6.09	22.0
h. 2. Chromhydroxid-Zugabe: 250 mg Cr/l				
nach 1 Tag	-	51.0	6.12	21.5
nach 2 Tag	-	51.7	6.14	22.0
nach 3 Tag	-	50.6	6.03	22.1
g. Chromnachweis im Klarwasserablauf stets negativ.				

- Key:
- a. Measurements
 - b. In synthetic effluent
 - c. In treated water (output)
 - d. In activation vessel
 - e. Consumption
 - f. pH
 - g. Chromium detection in treated water
always negative
 - h. Addition of chromium hydroxide

zu Beginn = at the beginning

nach = after

Tag = day

6. Series of Experiments with Chromosal B in the pH Range around 6.0; Rising Amounts of Chromium

The previous experiments did not resolve the question of whether the favorable results might not be attributable to the fact that the aging of the chromium hydroxide had already progressed so far that the "oily" hydroxide was resistant to the acidity of the effluent. For this reason, further experiments were conducted with soluble Chromosal B as in Series 3, the only

differences being that the pH was lowered from 7.5 to about 6.0, and that the Chromosal was added at 3-day (instead of 2-day) intervals.

Table 6

Experiments with increasing quantities of Chromosal B with pH about 6.0

Messungen a.	b. im synth. Abwasser KNO ₃ -Verbrauch (mg/l) e.	c. im Klärwasserablauf pH-Wert f.	Chrom- nach- weis g.	Im Belebungs- gerät d. Temp. (°C)
zu Beginn	183.6	-	-	21.5
nach 1 Tag	-	48.2	6.03	21.6
nach 2 Tag	-	49.2	6.05	21.6
h. 1. Chromzugabe: 100 mg Cr/l				
nach 1 Tag	-	50.6	5.96	neg.
nach 2 Tag	-	59.7	5.96	21.3
nach 3 Tag	-	51.2	6.01	21.3
h. 2. Chromzugabe: 100 mg Cr/l				
nach 1 Tag	-	52.0	6.03	neg.
nach 2 Tag	-	51.6	5.94	21.5
nach 3 Tag	-	50.2	5.92	21.6
h. 3. Chromzugabe: 100 mg Cr/l				
nach 1 Tag	-	53.6	5.95	3 mg
nach 2 Tag	-	54.9	6.05	3 mg
nach 3 Tag	-	53.0	6.10	2 mg
h. 4. Chromzugabe: 100 mg Cr/l				
nach 1 Tag	-	59.2	5.87	8 mg
nach 2 Tag	-	60.5	5.95	6 mg
nach 3 Tag	-	61.2	5.98	6 mg
h. 5. Chromzugabe: 100 mg Cr/l				
nach 1 Tag	-	65.7	5.95	19 mg
nach 2 Tag	-	65.0	6.01	16 mg
nach 3 Tag	-	66.7	6.09	15 mg

Key: a. Measurements
b. In synthetic effluent
c. In treated water (output)
d. In activation vessel
e. Consumption
f. pH
g. Chromium determination
h. Addition of chromium

zu Beginn = at the beginning
nach = after
Tag = day

The results (Table 6) show that soluble chromium was found in the treated water output in these experiments when more than 200 mg Cr/l was added. The

amounts of chromium discovered were relatively small by comparison with the total chromium input, but finally rose to 15-19 mg when 500 mg Cr/l was added. It is noteworthy, however, that the activated sludge obviously exerts adsorption forces on the chromium, the latter probably being bound to the proteins in the activated-sludge flakes. This conjecture is supported by the fact that, in the absence of activated sludge, a Chromosal solution set to a pH of 6.0, allowed to stand for 24 h, and then filtered contained about 85 mg/l in soluble form when 500 mg Cr/l was added, in contrast to only 15-19 mg when the solution was mixed with activated sludge. All in all, however, this series of experiments showed that even under these experimental conditions, the chromium concentration can be as much as 200 mg Cr/l without soluble chromium compounds appearing in the treated-water output and without any appreciable increase in the permanganate consumption relative to the control test. Even when the chromium concentration was raised still further, starting with the third addition, the decline in the activity of the activated sludge which was observed in this pH range near 6.0, which after all was not the optimum for the biological processes, was not particularly alarming in view of the very high chromium concentrations employed in this experiment.

7. Series of Experiments with Chromosal B Near pH 8.5 with Increasing Quantities of Chromium

As previously mentioned, the most favorable hydrogen ion concentration for the activated sludge procedure is between 7.2 and 7.4. Regardless of this fact, a series of experiments analogous to that described under 6 was conducted, the difference being that the pH of the effluent or of the activated-sludge system was set to 8.5 by adding NaOH. As can be seen from Table 7, the chromium compounds were not observed to have an detrimental

effects on the biological activity of the activated sludge in this pH range, this obviously being due to the fact that the chromium is completely precipitated as the hydroxide at pH 8.5, and thus occurs in a completely inactivated form. In this series of experiments as well, the activated sludge eventually assumed the typical green color of chromium hydroxide due to the large amounts of chromium added.

Table 7

Experiments with increasing amounts of Chromosal B near pH 8.5

Messungen a.	b. in synth. Klarwasser KNO ₃ -Verbrauch (mg/l) e.	c. in Klarwasser- ablauf pH-Wert f.	d. in Fällungs- gefäß Temp. (°C) g.
zu Beginn	173.1	-	20.5
nach 1 Tag	-	27.8	21.3
nach 2 Tag	-	29.0	22.0
1. Chromzugabe: 100 mg Cr/l			
h.			
nach 1 Tag	-	30.5	21.6
nach 2 Tag	-	30.0	21.8
nach 3 Tag	-	28.6	21.0
2. Chromzugabe: 100 mg Cr/l			
h.			
nach 1 Tag	-	29.1	21.3
nach 2 Tag	-	30.2	21.9
nach 3 Tag	-	27.9	21.4
3. Chromzugabe: 100 mg Cr/l			
h.			
nach 1 Tag	-	28.6	21.0
nach 2 Tag	-	30.9	21.5
nach 3 Tag	-	26.8	21.0
4. Chromzugabe: 100 mg Cr/l			
h.			
nach 1 Tag	-	27.9	20.9
nach 2 Tag	-	28.1	21.3
nach 3 Tag	-	30.2	21.6
5. Chromzugabe: 100 mg Cr/l			
h.			
nach 1 Tag	-	29.7	21.1
nach 2 Tag	-	27.6	21.5
nach 3 Tag	-	30.0	21.3
g. Chromnachweis in Klarwasserablauf stets negativ.			

Key: a. Measurements
b. In synthetic effluent
c. In treated water (output)
d. In activation vessel
e. Consumption
f. pH
g. Chromium determination in treated water (output) always negative

h. Addition of chromium
zu Beginn = at the beginning
nach = after
Tag = day

8. Experiments with Chrome Leather Buffing Dust

As already described in Series 4, appreciable quantities of chromium hydroxide do not normally reach the activated-sludge unit at all, since they are deposited in the preceding settling tank. This holds to an even greater degree for other impurities, such as animal hairs, shreds of tanned skin, and leather buffing dust, which can occasionally be found in tannery effluent along with other solids. Nevertheless, as part of this work, an attempt was made to determine whether chrome leather buffing dust might have unfavorable effects on the activity of the sludge due to its chromium content if some of it got into the activated-sludge plant.

The experiments were conducted with two different types of buffing dust, each with a different chromium content. The first had 1.0% Cr (Experiment A) and the second 2.4% Cr (Experiment B). In both series of experiments, the starting dose was 5 mg Cr/l effluents; further amounts of buffing dust, corresponding to 5 mg Cr/l each, were added at 3-day intervals. The maximum in each case was 25 mg Cr/l. This chromium content corresponded in the first case to 2500 mg buffing dust per liter, and in the second to 1040 mg/l. Hence, the total amounts of solid materials added were enormously high or completely unrealistic if they were to be compared with raw effluent flowing into a collective sewage-treatment plant, particularly for effluent which had undergone a preliminary treatment in an activated sludge tank. According to Appendix 1, Section 11 of the "Guidelines" [1] of the Husmann Committee, dumping solids which might block flow in the sewer system by depositing in the pipes is undesirable, and it would be very difficult to find a Water Department which would tolerate solids at levels like 1000 and 2500 mg/l raw effluent.

The values in Tables 8 and 9 show that chromium could never be detected in the treated water output from the activated sludge treatment. The chromium compounds were bound so strongly to the hide substance that they had no influence on the biological treatment. It just looks as if adding a new amount of buffing dust is accompanied by a slight increase in potassium permanganate consumption and a temporary, slight drop in pH. In the first case, this might be due to certain proportions of soluble organic substances, and in the second case, to the normal, natural acidity of the chrome buffing dust. Nevertheless, in view of the large amounts of buffing dust added, this effect is extremely small.

Table 8

A. Experiments with increasing amounts of buffing dust (chrome buffing dust with 1.0% chromium content, total amount added about 2500 mg buffing dust per liter effluent)

Messungen G.	in synth. Abwasser KNO ₃ -Versuch 4 (mg/l) e	in Klarwasser- ablauf C pH-Wert	in Belebungs- gefäß Temp. (°C)
zu Beginn	151.0	-	21.5
nach 1 Tag	-	52.5	7.35
nach 2 Tag	-	42.3	7.30
nach 3 Tag	-	41.9	7.32
1. Schleifstaub-Zugabe entsprechend 5 mg Cr/l			
nach 1 Tag	-	51.3	7.21
nach 2 Tag	-	50.6	7.25
nach 3 Tag	-	48.1	7.29
2. Schleifstaub-Zugabe entsprechend weitere 5 mg Cr/l			
nach 1 Tag	-	54.3	7.25
nach 2 Tag	-	48.9	7.22
nach 3 Tag	-	48.1	7.29
3. Schleifstaub-Zugabe entsprechend weitere 5 mg Cr/l			
nach 1 Tag	-	56.2	7.15
nach 2 Tag	-	53.1	7.18
nach 3 Tag	-	52.4	7.20
4. Schleifstaub-Zugabe entsprechend weitere 5 mg Cr/l			
nach 1 Tag	-	55.1	7.18
nach 2 Tag	-	56.3	7.16
nach 3 Tag	-	55.2	7.21
5. Schleifstaub-Zugabe entsprechend weitere 5 mg Cr/l			
nach 1 Tag	-	58.3	7.10
nach 2 Tag	-	57.2	7.16
nach 3 Tag	-	55.1	7.20
Chromnachweis im Klarwasserablauf stets negativ			

[Key on following page]

Key to Table 8

- a. Measurements
- b. In synthetic effluent
- c. In treated water output
- d. In activation vessel
- e. Consumption
- f. pH
- g. Chromium determination in treated water output always negative
- h. Addition of buffering dust corresponding to 5 mg Cr/l
- i. Addition of buffering dust corresponding to a further 5 mg Cr/l

zu Beginn = at the beginning

nach = after

Tag = day

C. Sludge Digestion/Gasification Experiments

Once it had been established that the overwhelming majority of chromium compounds present in tannery effluents were already in insoluble form -- whether in the primary sludge or in the sludge from the activated-sludge plant -- as long as the effluents had been properly neutralized to pH 6.5-9.5 in accordance with the instructions of the Husmann Committee, and as long as the activated sludge treatment was carried out in the usual pH range of 7-8, it now seemed particularly important to investigate the extent to which increasing concentrations of chromium compounds could affect the sludge treatment in the digestion tower.

The experiments were carried out in 2-l Woulff flasks, which were placed in rectangular, water-filled, heatable plastic tanks, the latter serving as thermostats and designed to accommodate four Woulff flasks at one time. One port in each flask was closed during the experiment, while the other was connected by a hose to a second, elevated, likewise water-filled, rectangular plastic tank, which can hold four inverted 1000-ml graduated cylinders to catch the methane evolved (Fig. 2). Since specific model sludges, as employed

Table 9

B. Experiments with increasing amounts of buffing dust (chrome buffing dust with 2.4% chromium content, total amount added about 1040 mg buffing dust per liter effluent)

Messungen a.	b. synth. Klarwasser- ablauf (mg/l)	c. in Klarswasser- ablauf (mg/l)	d. in Aktivierungs- gefäß Temp. (°C)	e. pH-Wert
zu Beginn	169.6	-	-	20.6
nach 1 Tag	-	94.3	7.42	21.0
nach 2 Tag.	-	92.1	7.45	21.4
nach 3 Tag.	-	81.5	7.50	21.2
1. Schleifstaub-Zugabe entsprechend 5 mg Cr/l				
nach 1 Tag	-	86.9	7.44	21.5
nach 2 Tag.	-	86.6	7.50	21.3
nach 3 Tag.	-	86.4	7.52	21.2
2. Schleifstaub-Zugabe entsprechend weitere 5 mg Cr/l				
nach 1 Tag	-	86.0	7.41	20.9
nach 2 Tag.	-	86.7	7.46	21.3
nach 3 Tag.	-	84.3	7.48	21.5
3. Schleifstaub-Zugabe entsprechend weitere 5 mg Cr/l				
nach 1 Tag	-	86.9	7.39	21.9
nach 2 Tag.	-	86.3	7.35	21.7
nach 3 Tag.	-	85.2	7.35	21.6
4. Schleifstaub-Zugabe entsprechend weitere 5 mg Cr/l				
nach 1 Tag	-	87.3	7.25	21.1
nach 2 Tag.	-	86.9	7.30	21.5
nach 3 Tag.	-	86.0	7.32	21.6
5. Schleifstaub-Zugabe entsprechend weitere 5 mg Cr/l				
nach 1 Tag	-	88.1	7.22	21.9
nach 2 Tag.	-	89.1	7.27	21.7
nach 3 Tag.	-	87.8	7.30	21.5
g. Chromnachweis in Klarwasserablauf stets negativ				

- Key:
- a. Measurements
 - b. In synthetic effluent
 - c. In treated water output
 - d. In activation vessel
 - e. Consumption
 - f. pH
 - g. Chromium determination in treated water output
always negative
 - h. Addition of buffing dust corresponding to 5 mg Cr/l
 - i. Addition of buffing dust corresponding to a further
5 mg Cr/l

zu Beginn = at the beginning
nach = after
Tag = day

by other authors in similar studies, were not available for these sludge digestion experiments, sludge from the digestion towers of the sewage-treatment plant of Reutlingen was used, whatever its composition at the time. The original intention of using a mixture of 1/3 digestion-tower sludge (as an inoculating sludge) and 2/3 fresh sludge directly from the settling tank (before being transferred to the digestion tank) had to be abandoned, because the evolution of gas became too violent, resulting in explosion-like events in the Woulff flasks employed. Therefore, from this point on, the sludge employed was taken from a perfectly functioning digestion tank.

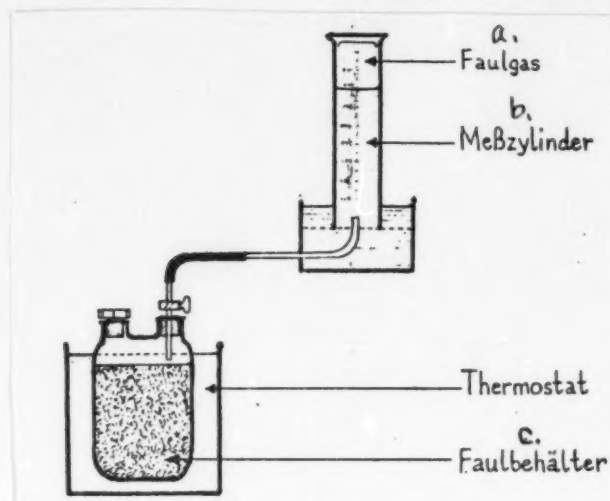


Fig. 2. Setup for sludge digestion experiments

Key: a. Methane
b. Graduated cylinder
c. Digestion tank

As part of the digestion experiments about to be described, the quantities of chromium compounds were varied as in the activated sludge experiments, and

the chromium compounds were again added to the sludge in the form of chrome alum, Chromosal B, chromium hydroxide, and chrome leather buffing dust. Temperature and pH were also varied. The sludge employed in the experiments was procured freshly for each series of experiments from the Reutlingen sewage-treatment system. Immediately upon being withdrawn from the digestion tank, it was filtered through a large screen with 1-2 mm mesh into the treatment plant, in order to remove large sludge particles, e.g. carried along from the settling tank into the digestion tower. Analytical studies to characterize the sludge generally included determining the dry weight, pH, and chromium content.

1. Series of Experiments with Different Digestion Chamber Temperatures and Different Chromium Supplements (25-50 mg Cr/l)

The decomposition of the sludge and the methane yield depend on a wide range of influences, among which the type and composition of the sludge, the temperature, and the pH are particularly important. Although practical experience in sludge digestion has shown that methane-producing bacteria work best at about 30°C, this work will include experiments at lower or higher temperatures, with simultaneous variations in the amount of chromium added at each selected experimental temperature. The experimental temperatures were 20°, 32°, and 54°C, and the chromium compound was again Chromosal B. The duration of the experiment was 14 days for each series, and the chromium concentrations were 25, 50, and 100 mg Cr/l sludge. In order to permit direct comparisons, the same sludge with the same percentage of dry substance was employed in all temperature-variation experiments.

As Table 10 shows, the most favorable gas yield was actually obtained at 32°C. Accordingly, all further investigations were conducted at this

Table 10

Sludge digestion experiments with varying digestion tower temperature and different amounts of chromium added in the form of Chromosal B (14 days). Dry residue of sludge: 39,500 mg/l

a.	angewandte Chrommenge	0	25	50	100
b.	mg/l Faulschlamm				
c.	% auf Schlammtrokergesubstanz	0	0,06	0,125	0,253
d. Versuchstemperatur 20°C					
e.	pH-Werte	7,52	7,50	7,51	7,48
f.	Gesamt-Gasmenge ml	4900	4895	4880	4790
g.	Gasausbeute %, bezogen auf den Blindversuch	100	99,9	99,6	97,8
d. Versuchstemperatur 32°C					
e.	pH-Werte	7,55	7,53	7,56	7,50
f.	Gesamt-Gasmenge ml	6130	6115	6075	5897
g.	Gasausbeute %, bezogen auf den Blindversuch	100	99,7	99,1	96,4
d. Versuchstemperatur 54°C					
e.	pH-Werte	7,53	7,60	7,62	7,58
f.	Gesamt-Gasmenge ml	5205	5125	4975	4820
g.	Gasausbeute %, bezogen auf den Blindversuch	100	96,9	94,1	91,2

Key: a. Amount of chromium employed
 b. mg/l sludge
 c. Percent with respect to dry weight of sludge
 d. Experiment temperature
 e. pH
 f. Total quantity of gas in ml
 g. Gas yield in percent, relative to control test

temperature. The Reutlingen sewage-treatment plant, the source of the sludge employed here, as well as plants in other locations operate at this temperature of 32°C. As for the chromium dose, it was found that increasing the chromium content up to 100 mg Cr/l did affect the gas yield to a certain extent, but at the normal digestion temperature (32°C), the maximum decrease in gas yield relative to the control experiment without chromium was only 3.6%. At 20°C, the reduction was even less (2.2%), while at a higher temperature

(54°C), a gradually rising chromium influence on the gas yield was observed. Even this, however, was only about 9% with 100 mg Cr/l. It is noteworthy that chromium components were not detected in any of the sludge filtrates at the conclusion of the experiment, so that it can be assumed that the biological impairment of the sludge digestion system or of the methane gas bacteria, etc. may have occurred less during the progress of the experiment than right at the beginning of the experiment when the Chromosal was added, at a point when the chromium compounds were still in soluble form. Practical experience in biological sewage treatment has in fact shown that sudden "surges" of effluent with biologically harmful impurities or ingredients have particularly detrimental effects on the microorganisms. This was also corroborated by the experiments in Section 4.

2. Series of Experiments with Different Digestion Chamber pH's and Different Chromium Supplements (50-200 mg Cr/l)

This series of experiments dealt with variations of pH in the digestion chamber, although the optimum pH for sludge digestion has been empirically determined to be in the essentially neutral range (up to about 8.0). The pH in the experiments was 6.0, 7.5, and 9.0 at a single experiment temperature of 32°C, and always using the same sludge. Moreover, the amount of Chromosal added was raised in stages to 200 mg Cr/l sludge.

As can be seen from Table 11, the maximum gas yield was found as expected at pH 7.5, and the lowest at pH 9.0. In the control tests without any addition of chromium, the decrease in gas yield at pH 6.0 from that at pH 7.5 was 29.4%, while the decrease at pH 9.0 from pH 7.5 was actually 41.9%. On the other hand, the reduction in gas yield brought about by adding chromium salts was considerably less. When adding 200 mg Cr/l sludge, it was

Table 11

Sludge digestion experiments with varying digestion tower pH and with varying amounts of chromium added in the form of Chromosal B (21 days)
Dry residue of sludge: 38,400 mg/l; experiment temperature 32°C

a.	angewandte Chrommenge				
b.	a) mg/l Faulschlamm	0	50	100	200
c.	b) % auf Schlamm-trocken-substanz	0	0,11	0,26	0,52
d. pH etwa 6.0					
e.	pH-Werte	6,05	6,15	6,08	5,97
f.	Gesamt-Gasmenge ml	5445	4815	4545	4265
g.	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	88,4	83,5	78,3
d. pH etwa 7.5					
e.	pH-Werte	7,58	7,57	7,55	7,52
f.	Gesamt-Gasmenge ml	7725	7640	7370	7175
g.	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	98,9	95,4	92,9
d. pH etwa 9.0					
e.	pH-Werte	8,95	9,02	9,05	9,01
f.	Gesamt-Gasmenge ml	4490	4500	4445	4405
g.	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	100,2	99,0	98,3
h.	Chromnachweis in Schlammfiltrat stets negativ				

Key: a. Amount of chromium employed
b. mg/l sludge
c. Percent with respect to dry weight of sludge
d. pH about
e. pH
f. Total quantity of gas in ml
g. Gas yield in percent, relative to control test
h. Chromium determination in sludge filtrate
always negative

1.7% in comparison with the control test without any added chromium at pH 9.0 and only 7.1% at pH 7.5. The drop in gas yield brought about by adding chromium compounds was greatest at pH 6.0 (21.7%), since in this pH range, the chromium will not have flocculated out completely as the hydroxide. It is noteworthy, however, that soluble chromium fractions were not found in any of the sludge filtrates after the digestion experiments were concluded, even

at pH 6.0, all the chromium instead obviously being bound to the sludge. We will return to this phenomenon at a later point. Based upon these results, all further experiments were conducted at pH 7.5.

3. Series of Experiments with Variations in Quantities of Chromium Salts Added in the Form of Chromosal or Chrome Alum

Under the pH and temperature conditions established as the optimum ones by the results of the preceding experiments, two new series of experiments were now conducted using Chromosal B and chrome alum, adding 25, 50, and 100 mg Cr/l to the sludge in the first series, and 300, 600, and 1200 mg in the second. In the first series with lower amounts of chromium, the same sludge with 39,690 mg dry weight per liter was employed, while another sludge with 46,740 mg dry weight per liter was employed in the second series of experiments with up to 1200 mg Cr/l.

As can be seen from Tables 12 and 13, the gas yields in these experiments also gradually declined, as expected, as the chromium content in the sludge increased, the differences between Chromosal B and chrome alum being very slight. Under the conditions of these series of experiments, the drop in gas yield was about 5% when 100 mg Cr/l was added to the sludge, and 7-10% with 300 mg Cr/l. It took considerably higher dosages to bring about substantial gas losses (18-20 and 24-27%), although even in these experiments, i.e. even when 1200 mg Cr/l was added in the form of Chromosal or chrome alum, no soluble chromium compounds were detected in the sludge filtrates. The impairment of the effectiveness of the system can probably be found in the initial stages in this case as well, at a time when the chromium compounds are still in soluble form or when the resulting chromium sludges are still not sufficiently oily. In that case, these observations can easily be explained

Table 12

Sludge digestion experiments with various quantities of chromium salts added (21 days). Dry residue of sludge: 39,690 mg/l; pH in digestion tower about 7.5; experiment temperature 32°C.

a.	angewandte Chrommenge				
b.	a) mg/l Faulschlamm	0	25	50	100
c.	b) % auf Schlamm- Trockensubstanz	0	0,06	0,12	0,25
Chromosal B					
d.	pH-Werte	7,67	7,65	7,62	7,63
e.	Gesamtgasmenge ml	7680	7660	7600	7260
f.	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	99,7	98,8	94,5
Chromalaun h.					
d.	pH-Werte	7,65	7,61	7,60	7,55
e.	Gesamtgasmenge ml	6685	6695	6650	6340
f.	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	100,2	99,5	94,8
g.	Chromnachweis im Schlammfiltrat stets negativ				

Table 13

Sludge digestion experiments with addition of large quantities of chromium salts (14 days). Dry residue of sludge: 46,740 mg/l; pH in digestion tower about 7.5; experiment temperature 32°C.

a.	angewandte Chrommenge				
b.	a) mg/l Faulschlamm	0	300	600	1200
c.	b) % auf Schlamm- Trockensubstanz	0	0,66	1,32	2,64
Chromosal B					
d.	pH-Werte	7,61	7,58	7,54	7,57
e.	Gesamtgasmenge ml	7845	7315	6465	5960
f.	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	93,2	82,4	75,9
Chromalaun h.					
d.	pH-Werte	7,46	7,42	7,46	7,41
e.	Gesamtgasmenge ml	8240	7740	6605	6065
f.	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	90,3	80,0	73,6
g.	Chromnachweis im Schlammfiltrat stets negativ				

[Key to Tables 12 and 13 on following page]

Key to Tables 12 and 13

- a. Amount of chromium employed
- b. mg/l sludge
- c. Percent relative to dry weight of sludge
- d. pH
- e. Total amount of gas in ml
- f. Total gas yield in percent, relative to control test
- g. Chromium determination in sludge filtrate always negative
- h. Chrome alum

by supposing that some of the sludge-digesting bacteria, which after all are organisms made of protein, undergo a type of tanning due to the Chromosal or chrome alum, and this effect brings about a reduction in the biological activity of the sludge involved. We will return to this aspect at a later point.

4. Series of Experiments with Chromium Formate

It is known from the practice of chrome tanning that selecting salts of organic acids with strong tendencies to form complexes and adding them to chromium sulfate solutions produces tanning liquors in which the chromium is present in so-called masked form. In this case, the chromium precipitates very slowly if at all when alkali or ammonia is added, and the originally purely cationic chromium complexes simultaneously take on an anionic charge, while the tanning power for animal hides decreases. The next series of experiments was designed to discover the extent to which such "masked" chromium compounds exert an influence on sludge digestion. For this purpose, 0.658 kg sodium formate was added for each kg of chromic oxide (in the form of a Chromosal solution), where it can be assumed that most of the formate is incorporated into the chromium complex. This assumption was confirmed by the observations of this series of experiments, the results of which are contained in Table 14.

Table 14

Sludge digestion experiments using chromium compounds masked by addition of formate (21 days). Dry residue of sludge: 37,650 mg/l; pH in digestion tower about 7.5; experiment temperature 32°C

a.	angewandte Chrommenge	0	125	250	500
b.	a) mg/l Faulschlamm				
c.	b) % auf Schlammtrökensubstanz	0	0,33	0,66	1,32
d.	pH-Werte	7,42	7,48	7,45	7,50
e.	Gesamtgasmenge ml	8605	8595	8585	8325
f.	Gesamtgasausbeute %, bezogen auf den Bliriverauch	100	99,8	99,7	96,7
g.	Chromnachweis in Schlammfiltrat stets negativ				

- Key:
- a. Quantity of chromium employed
 - b. mg/l sludge
 - c. Percent with respect to dry weight of sludge
 - d. pH
 - e. Total amount of gas in ml
 - f. Total gas yield in percent, with respect to control experiment
 - g. Chromium determination in sludge filtrate always negative

In the case of chromium compounds masked by adding formate, the amount of chromium could be raised to as much as 500 mg Cr/l sludge before the gas yield fell by 3.3%. When unmasked chromium (as Chromosal B) was used, as in Series 3 (Table 12), the gas yield had already dropped by 5.4% at a dosage of 100 mg Cr/l sludge. This series of experiments therefore supports the inference that while temperature and pH are important, it is not just the absolute quantity of chromium gaining access to the sludge which counts, but also, very strongly, the form in which the chromium compounds enter the digestion tower. Using more or less masked chrome liquors, as is frequently

done in practice, therefore has a favorable effect on the conditions for sewage treatment.

5. Series of Experiments with Addition of Increasing Quantities of Chromic Hydroxide

One discrepancy between actual conditions in sludge digestion and the conditions under which the previous experiments were conducted was that the chromium compounds in all the experiments were added in soluble form (chrome alum, Chromosal, masked chromium salts) and were not precipitated until that point. In practice, however, the chromium compound in the sludge, whether primary sludge or sludge coming from the activated-sludge plant into the digestion tower, are already present in insoluble form as oil-covered chromium hydroxide or highly basic chromium sulfate. In this form, the chromium is indifferent from the very beginning. Once the experiments on the activated sludge method had shown that chromium in this form does not interfere with the biological sewage treatment at all, it was reasonable to assume that the same should hold for sludge digestion as well. We therefore decided to conduct further experiments, adding aged and thus more or less oily chromium hydroxide, i.e. in the form in which the chromium normally occurs in the effluent sludge. In this series, the temperature was again 32°C, the pH was about 7.5, and the hydroxide doses corresponded to 16, 80, 400, 800, 1600, and finally even 3200 mg Cr/l sludge. The hydroxide was prepared in a manner analogous to that in the activated sludge experiments, and was therefore aged for about 3 weeks. However, as can be seen from Table 15, even the highest hydroxide does did not bring about a decline of more than 0.5% in the gas yield, as compared with the chromium-free control test, when the total digestion time was 3 weeks.

Table 15

Sludge digestion experiments with addition of increasing amounts of chromic hydroxide (21 days). Dry residue of sludge: 31,500 mg/l; pH in digestion tower about 7.5; experiment temperature 32°C.

a.	angewandte Chrommenge	0	16	80	400
b.	a) mg/l Faulschlamm				
c.	b) % auf Schlammtrö-				
d.	cken-substanz	0	0,05	0,25	1,25
e.	pH-Werte	7,42	7,43	7,58	7,56
f.	Gesamtgasmenge ml	4525	4495	4535	4505
	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	99,3	100,2	99,6
a.	angewandte Chrommenge	0	800	1600	3200
b.	a) mg/l Faulschlamm				
c.	b) % auf Schlammtrö-				
d.	cken-substanz	0	2,50	5,00	10,00
e.	pH-Werte	7,50	7,52	7,57	7,60
f.	Gesamtgasmenge ml	4250	4255	4210	4230
	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	100,1	99,1	99,5
g.	Chromnachweis im Schlammfiltrat stets negativ				

Key: a. Quantity of chromium employed
 b. mg/l sludge
 c. Percent with respect to dry weight of sludge
 d. pH
 e. Total amount of gas in ml
 f. Total gas yield in percent, with respect to control experiment
 g. Chromium determination in sludge filtrate always negative

These findings show that if trivalent chromium were eventually discovered to be toxic, it would not be the total amount of chromium in the sludge which was important, but rather the type and chemical history of the chromium compounds involved. The conditions would obviously be most favorable when the chromium entered the digestion tower in flocculated and very oily form from the very beginning, as in these experiments, i.e. in the only form occurring in the practice of sewage treatment. In this form, which is also highly resistant to a sudden influx of acidic effluent, interaction with the

sludge-digesting bacteria can be practically ruled out, on the basis of this series of experiments.

6. Series of Experiments with Addition of Varying Amounts of Chrome Leather Buffing Dust

Lastly, as indicated by previous remarks, it must be anticipated that certain amounts of buffing dust may be present in the sludge digestion method. This is in contrast to the activated sludge method, in which such coarse mechanical components are usually precipitated by sedimentation in the preceding settling tank. Because of this possibility, it was vital to investigate this point as well. In the experiments of this series (32°C, pH 7.5), three buffing dusts of different compositions were employed, the respective chromium contents being about 1.0, 3.0, and 4.0%.

The results in Table 16 show that with increasing quantities of buffing dust, despite the associated rise in chromium content, the gas yield did not decrease, but instead increased very strikingly, and that even abnormally large quantities of buffing dust which would be hardly realistic in practice did not cut the gas yield but instead raised it. This was never a result of acidic fermentation, since the pH values in all the tests were still close to 7.5, even after 3 weeks. This rise was largest for the buffing dust with the lowest chromium content, and therefore the lowest tanning intensity. This effect is undoubtedly due to the fact that the hide substance in the leather is attacked by the microorganisms, generating additional amounts of gas.

D. Summary

The objective of these investigations was to discover whether and at which concentrations the dissolved or undissolved chromium compounds in the

Table 16

Sludge digestion experiments with addition of varying amounts of chrome leather buffing dust (21 days). pH in digestion tower about 7.5; experiment temperature 32°C.

a.	Chromgehalt des Schleifstaubes rund 1% Cr;				
b.	Trockenrückstand des Schlammes: 35.73% w/w				
c.	angewandte Chrommenge				
d.	a) mg/l Faulschlamm	0	30	60	120
e.	b) % auf Schlamm-trocken-substanz	0	0.082	0.165	0.33
f.	pH-Werte	7.36	7.42	7.45	7.30
g.	Gesamt-Gasmenge ml	3405	4950	5625	6050
h.	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	144	165	177
i.	Blindversuch				
a.	Chromgehalt des Schleifstaubes rund 3% Cr;				
b.	Trockenrückstand des Schlammes: 16.0% w/w				
c.	angewandte Chrommenge				
d.	a) mg/l Faulschlamm	0	30	150	300
e.	b) % auf Schlamm-trocken-substanz	0	0.25	0.50	1.00
f.	pH-Werte	7.65	7.70	7.68	7.66
g.	Gesamt-Gasmenge ml	4522	5140	5545	7725
h.	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	111	120	167
i.	Blindversuch				
a.	Chromgehalt des Schleifstaubes rund 4% Cr;				
b.	Trockenrückstand des Schlammes: 40.72% w/w				
c.	angewandte Chrommenge				
d.	a) mg/l Faulschlamm	0	100	200	400
e.	b) % auf Schlamm-trocken-substanz	0	0.25	0.50	1.00
f.	pH-Werte	7.52	7.60	7.61	7.53
g.	Gesamt-Gasmenge ml	3155	3615	4225	4625
h.	Gesamtgasausbeute %, bezogen auf den Blindversuch	100	115	134	153
i.	Blindversuch				
j.	Chromnachweis in Schlammfiltrat stets negativ				

- Key:
- a. Chromium content of buffing dust about ...
 - b. Dry residue of sludge
 - c. Amount of chromium employed
 - d. Sludge
 - e. With respect to dry weight of sludge
 - f. pH
 - g. Total quantity of gas
 - h. Total gas yield in percent, relative to control test
 - i. Chromium determination in sludge filtrate always negative

effluents of the leather industry could have detrimental effects on the biological treatment of the effluent itself and on sludge digestion. Based on the results of these investigations, the following conclusions can be made:

1. Activated Sludge Process

1.1. If, as is customary, an activated sludge plant operates at a pH between 7.0 and 8.5, the chromium concentration can be increased to 500 mg Cr (III)/l effluent, without affecting the biology at all. In this pH range, it makes no difference whether this chromium is added in the form of already aged insoluble chromium hydroxide sludge or in the form of soluble chromium compounds, since at a pH of 7 or more, the soluble chromium compounds precipitate in insoluble form immediately upon addition.

1.2. The same is true when insoluble chrome leather buffing dust is added. As much as 2500 mg buffing dust/l effluent can be added without impairing the biology, since the chromium compounds are bound firmly to the collagenic hide substance.

1.3. If the pH in the activated sludge plant is lowered to 6, addition of as much as 500 mg Cr/l effluent likewise has no detrimental effect on the biology, as long as the chromium is added in the form of already precipitated and aged chromium hydroxide sludge. If, on the other hand, the chromium is added in the form of soluble salts, quantities greater than 200 mg Cr/l effluent bring about a certain decrease in activity in the activated sludge process, since the chromium is no longer completely precipitated and chromium was found in the treated water output. However, in a properly run activated sludge plant, this case cannot arise, since

1.3.1. the pH in such plants should never drop below 7.0, and

1.3.2. neutral or alkaline conditions should prevail in either the mixing tank of the tannery or the mixing tank of the treatment plant, so that virtually all the chromium compounds will be precipitated in insoluble form and will thus remain in the primary sludge so that they cannot get into the activated sludge plant.

1.4. Interesting in this connection are the results of effluent studies carried out in 1968 at our Institute. At that time, 60 complete effluent studies were conducted by 20 leather factories in connection with an effluent survey of the Association of the German Leather Industry. Daily mixed samples were taken from these effluents on three days of the week in accordance with uniform procedures. Among other things, these samples, both filtered and unfiltered, were analyzed for chromium contents. The following results were obtained, with mean values in parentheses:

a. Art der verarbeiteten Rohware	b. Art der Gerbung	c. Chromgehalt (mg/l Mischabwasser)	
		unfiltriert d.	filtriert e.
f. Rindhäute	i. reine Chrom- gerbung	27—328 (104)	12—34 (19)
f. Rindhäute	j. chrom-pflanzlich kombiniert	23—341 (81)	11—199 (34)
g. Kalbfelle	i. reine Chrom- gerbung	110—247 (199)	6—12 (9)
h. Kleintierfelle	i. reine Chrom- gerbung	10—219 (34)	10—133 (39)

Key: a. Raw material
 b. Type of tanning
 c. Chromium content (mg/l mixed effluent)
 d. Unfiltered
 e. Filtered
 f. Cowhide
 g. Calfskin
 h. Skins of small animals
 i. Pure chrome tanning
 j. Combined chrome and vegetable tanning

This survey shows first that the chromium content was never as large as 500 mg Cr/l effluent and second that the chromium compounds in normal mixed tannery effluent are largely in the insoluble state already, since the mixed effluents from tanneries are normally more or less alkaline. Therefore, most of the chromium compounds in tannery effluents, just like the chrome buffing

dust, do not get into the activated sludge tank at all, but pass directly into the sludge digestion plant through the primary sludge. If they do get into the activated sludge tank, they are either in insoluble form, and thus harmless, or else the dissolved component is so small that no damage would be anticipated from it.

2. Sludge Digestion Process

2.1. The most favorable gas yield was obtained at temperatures around 30-32°C and pH 7-8, i.e. under the normal conditions for this process.

2.2. Under these operating conditions, chromium compounds in the form of insoluble chromium hydroxide sludge could be added in quantities up to 3200 mg Cr/l sludge = 10% chromium (relative to dry weight of sludge) without bringing about any observable disturbances in the bacteriology.

2.3. If the chromium compounds were added in the form of soluble chromium salts, then adding 100 mg Cr/l sludge = 0.25% Cr by dry weight decreased the gas yield by about 5%, while adding 300 mg Cr/l sludge = about 0.7% Cr by dry weight caused a decline in the gas yield by about 7-10%. However, it must be observed that these figures refer only to the eventuality that the chromium compounds reach the digestion tower in soluble form and do not precipitate until they reach the neutral or weakly alkaline conditions in the digestion tower. This case should seldom if ever occur in practice, since normally the chromium reaching the digestion tower is already in insoluble and rather rather heavily oiled form, and soluble chromium compounds will be present enclosed in the sludge in at most very small quantities.

2.4. It was possible to add chrome leather buffing dust in amounts of up to 1/3 of the dry weight of the sludge without giving rise to any observable impairment in the biology. Since there was a simultaneous increase in the

content of digestable organic materials, adding chrome leather buffing dust actually caused a substantial increase in gas output.

2.5. One finding relevant on this point is that the chromium content in pure tannery sludges normally varies between 1.2 and 1.7% by dry weight, as determined by our own investigations and the results of questionnaires. Once we had discovered that as much as 10% chromium, relative to dry weight, could be added to the sludge digestion process without impairing the biology, as long as the chromium compounds had been precipitated out in advance and the pH was properly controlled, a comparison of these values showed that essentially it would even be possible to pass tannery sludges directly and undiluted into the digestion tower, without causing difficulties in the biology, to the extent that these difficulties would originate in the chromium content (see below).

3. Conclusions

The results of this work summarized above are not unexpected. They permit the conclusion that trivalent chromium compounds probably have no "toxic effect" at all on the microorganisms involved in biological sewage treatment and sludge digestion. However, they are capable of tanning proteins, and since the microorganisms are protein-based, there is an interaction in this case as well, killing the microorganisms or reducing their activity. The occurrence of such a tanning effect presumes, however, that the chromium compounds will be present in soluble form. If they are insoluble, in the form of rather heavily oiled hydroxide sludge, or, in the case of chrome buffing dust, bound firmly to hide substance, a tanning effect is precluded, so that insoluble chromium compounds can be added even in extremely high doses, without impairing the biology in the activated sludge process or in the

sludge digestion process. If the chromium compounds are added in soluble form and if the pH is properly greater than 7 in the biological treatment process, again no impairment of the biology was observed, since the precipitation of chromium hydroxide takes place much faster than any possible tanning interaction with proteins. Of course, when large quantities of soluble chromium compounds are added, a certain tanning effect cannot be ruled out completely, particularly when the pH in the biological treatment process is pushed into the acid range. Normally, however, this case cannot occur, particularly when

1. the requirement of the Husmann Committee that the pH be between 6.5 and 9.5 for mixed tannery effluents as well as for all other effluents which reach the treatment plant is satisfied so that the chromium compounds introduced will be completely or largely insoluble,

2. the pH is held in the optimum range between 7.2 and 8.0 for the biological treatment of the effluent.

If this is the case, then even high concentrations of chromium compounds in tannery effluents should not have any detrimental effects on the biological treatment of the effluent or of the sludge.

From these studies, it can be concluded that the results of other Institutes mentioned at the outset -- dismissing any influence at all of trivalent chromium compounds on the biological treatment of effluent under normal conditions -- has been essentially confirmed. It is not just the total amount of chromium introduced into the activated-sludge or sludge-digestion system which is important, but also the form in which these chromium compounds are introduced, and since this fact was not always allowed for in previous investigations, the conflicting literature figures become at least partially understandable.

The results of this work also demonstrate that the limit of 4 mg Cr, dissolved and undissolved, per liter of raw effluent as given in the "Guidelines" of the Husmann Committee for trivalent chromium compounds is too stringent. As far as the content of chromium compounds is concerned, tannery effluents do not give rise to any special problems. From the chromium standpoint, the tannery effluents and the resulting sludge could be passed directly and undiluted into the activated sludge plant and the sludge digestion system without causing any difficulties. Of course, this is not the goal. Instead, it will always be preferable to treat tannery effluents together with other effluents, particularly residential sewage. This is because the reliability of the correct treatment is always much greater for mixed effluents, and the polycultures of microorganisms are much less vulnerable. Nevertheless, such a comparison is of great interest in this assessment. These studies have shown, however, that, as long as the pH of the mixed tannery effluent is properly controlled, substantially higher concentrations of chromium compounds can be tolerated without having to expect an harmful influences if the treatment plants are properly run. Naturally, the leather industry will take all practical technological measures to reduce the concentration of chromium compounds in effluents, since these tanning agents are expensive, and we will devote renewed attention to this question in a further research project. On the other hand, the leather industry should not be burdened with requirements which are not justified by the facts.

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